

of osmotic pressures in plants and animals, chemotaxis, the theory of ionisation and its application to the germicidal action of disinfectants, the permeability of membranes and the influence of this on secretion, the velocity of reactions, catalysis, colloidal solutions, and the bearing of physical chemistry on serum therapy, in which connection the work of Ehrlich, Arrhenius, and Madsen is briefly reviewed. Altogether this book supplies a decided want, and can be thoroughly recommended.

LETTERS TO THE EDITOR.

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Osmotic Pressure.

IN the issue of NATURE for May 3 (p. 19) appeared an abstract of a recent paper by Prof. Kahlenberg on "Osmosis and Osmotic Pressure." In Prof. Kahlenberg's paper, and also in the abstract, it is claimed that his experiments invalidate van 't Hoff's theory of osmotic pressure, by which the concordance between the pressure of gases and the osmotic pressure of dilute solutions was established. As the basis of that theory seems sometimes to be misunderstood, may I be allowed to recall the principles on which it is founded?

In a paper published in the *Zeitschrift für physikalische Chemie* for 1887, van 't Hoff showed that, from the well-known experimental relation between the solubility of a gas and the pressure, it followed by a simple application of the second law of thermodynamics that the osmotic pressure of a dilute solution must possess the same value as the ordinary pressure of a gas at the same concentration. The solution must be so dilute that the dissolved systems, each made up of a particle of solute as nucleus, and the portion of solvent which it influences, are beyond each others' spheres of action. The proof has been put in a modified form by Lord Rayleigh (NATURE, 1897), and Prof. Larmor has obtained the same result by using the fundamental conceptions of the molecular theory as a basis, instead of the experimental solubility relations of a gas (Phil. Trans., A, 1897). In all these proofs no assumption is made as to the nature of osmotic pressure. It may be due to molecular impacts or to chemical affinity, or to some other undiscovered cause. The strength (and weakness) of a thermodynamic proof lies in this very independence of assumptions as to the mechanism by which the effects are produced. Prof. Kahlenberg and his followers seem to consider that the thermodynamic theory of solutions stands or falls with the hypothesis that the pressure is due to molecular bombardment.

If the conditions assumed in the proofs are realised, the whole authority of thermodynamics goes to support the result. The importance of experiments on osmotic pressure, such as those of Prof. Pfeffer, Lord Berkeley and Mr. Hartley, and Prof. Kahlenberg, lies in the question how far the assumptions made in the thermodynamic proofs can be realised experimentally. This is a much humbler rôle than that assigned to the experiments by Prof. Kahlenberg, who claims that the application of gas laws to solutions is based on the few observations of Pfeffer and others by which those laws have been verified directly. Nevertheless, the experiments are of great interest. The gas value for the osmotic pressures measured by Pfeffer shows that the conditions laid down in the thermodynamic theory are realised in practice: (1) that for sugar solutions in water an approximately perfect semi-permeable membrane has been obtained; (2) that no selective action such as could be produced by a Maxwellian daemon is in operation; (3) that the molecules of cane sugar in solution are the simple molecules indicated by the chemical formula, though they may or may not be combined with solvent molecules; (4) that a solution which is dilute in the thermodynamic sense can

be realised at possible concentrations; (5) that a theory deduced for volatile solutes may be extended to other cases. When other solutions and different membranes are employed, one or more of these conditions may fail, and the theoretical value be beyond the reach of experimental attainment. Prof. Kahlenberg remarks that because a semi-permeable membrane does not exist, a theory which postulates one cannot be maintained. We might construct a parallel statement by saying that because a frictionless piston is not practically obtainable, in Carnot's engine and the science of reversible thermodynamics physicists and engineers have imagined a vain thing.

But I may point out that at least two perfect semi-permeable surfaces are probably known: (1) when a solution freezes to give the solid of the pure solvent, the solid is compressed into a smaller volume of liquid solution; the surface of the growing crystals is semi-permeable. (2) When a volatile solvent evaporates from the solution of a non-volatile solute, the free surface of the liquid is again a semi-permeable membrane. From these two facts follows the validity of the thermodynamic relations between the osmotic pressure on the one side and the freezing point and vapour pressure on the other. This is important, for it enables us to use measurements of freezing points or vapour pressures when it is not possible to realise the experimental conditions necessary for a satisfactory determination of the true osmotic pressure.

Osmotic pressure is a thermodynamic conception. The pressures observed in practice may or may not represent the same thing. We may define osmotic pressure as the excess of hydrostatic pressure it is necessary to exert on a solution in order that it may be in equilibrium with the solvent through a perfect semi-permeable membrane. With this definition we may use the conception of osmotic pressure as a basis for a Carnot's cycle and a thermodynamic theory of solutions. Prof. Kahlenberg writes that opponents of van 't Hoff's idea have generally held that the so-called osmotic pressure is an ordinary hydrostatic pressure, brought about by the entrance of liquid into the osmotic cell. It is delightful to find one point at least in which the supporters of van 't Hoff, and van 't Hoff himself, are in complete agreement with his opponents.

In the abstract of Prof. Kahlenberg's paper which appeared in NATURE we are warned that, among the general ruin of physical theories which is to follow his experiments, the hypothesis of ionic dissociation is involved. I confess that the warning leaves me unmoved. The idea that the ions of electrolytic solutions are dissociated from each other during their movement (though possibly or probably combined with the solvent) is required by the electrical phenomena. The abnormally great osmotic pressures of certain electrolytes dissolved in water indicate some kind of dissociation, but cannot tell us whether or not that dissociation takes place so as to give rise to electrified systems. In simple salts such as potassium chloride, which we know by their electrical properties to be electrically dissociated, it is difficult to see how a second kind of simultaneous dissociation could occur. But that non-electrical separation is sometimes found is indicated by some older experiments of Prof. Kahlenberg himself, who found that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, but are non-conductors of electricity. The theory of ionic dissociation rests upon electrical evidence, and by such evidence it must be tried.

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Trinity College, Cambridge, May 12.

CONSIDERABLE importance seems to be attached to a recent paper by Prof. Kahlenberg on "Osmosis and Osmotic Pressures" (*Jour. Phys. Chem.*, vol. x.), as is evidenced by a separate summary published in NATURE (May 3, p. 19). In these circumstances it may not be out of place to point out that the conclusions Prof. Kahlenberg deduces are not warranted.

On p. 142 he says "indirect measurements of osmotic pressures . . . from vapour tensions . . . involves the assumption that the gas laws hold for solutions." This is contrary to fact. We have shown experimentally (see vol. lxxvii. Proc. Roy. Soc.) that aqueous solutions of cane sugar give the same osmotic pressure whether observed

directly or deduced indirectly from their vapour pressures, and the relation connecting the osmotic and vapour pressures is quite independent of the "gas laws holding for solutions."

Leaving out of consideration the experiments made before the solutions were stirred—for on Prof. Kahlenberg's own showing these are not good—his conclusion that the gas laws do not hold for dilute solutions in pyridine is based on four experiments. If one may take No. 59 (p. 201) as a type of these, it is easy to show that the experiment is valueless.

The sugar solution used is 0.125 grm. mol. per litre, and a pressure of 98 cm. of mercury is reached, but the theoretical value is some 3 atmos. Now on p. 184 the diameter of his gauge is given as 0.5 mm., and he says that at the end of three days 0.115 grm. sugar has come through the membrane—this quantity represents 2.8 c.c. of solution. If we assume that this volume of solution came through the membrane at a uniform rate, a simple calculation will show that the rate is equivalent to a fall of 20 cm. *per hour* in the gauge. No wonder the theoretical pressure was never reached!

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BERKELEY.

E. G. J. HARTLEY.

Diurnal Variation of the Ionisation in Closed Vessels.

IN his letter on this subject published in NATURE of May 3 (p. 8) Mr. G. C. Simpson is, I venture to think, under a misapprehension regarding the conditions which determine the variations of the earth's electric field. His statement of the problem, which I have slightly abbreviated, is as follows:—"It is usual to accept that there is a negative charge on the earth's surface, and the corresponding positive charge is a volume charge distributed in the atmosphere. There is very little volume charge in the air close to the earth's surface, so the relation between potential gradient and charge on the earth's surface is given by $dv/dh = -4\pi\sigma$. Hence it follows that with a given charge on the earth's surface and the corresponding charge in the atmosphere above, the vertical distribution of the charge and the conducting state of the upper atmosphere do not in the slightest affect the potential gradient within a few metres of the earth's surface."

All this is very true, but it is equally true that *with a constant charge on the earth's surface* nothing whatever will affect the potential gradient close to it. Since the potential gradient is a constant multiple of the surface density, it is absurd to consider the variation of the one whilst the other is kept constant. The only assumption that it seems safe to make about the state of the earth's surface is that, owing to the relatively high conductivity of the earth's crust, for purposes of atmospheric electricity it may be treated as an equipotential surface. The charge in any particular region will be determined by the distribution of electrification and ionisation in the atmosphere, and will readjust itself almost instantaneously when any change takes place in the external conditions. It will not, as an incautious reader might gather from Mr. Simpson's letter, behave as if it were glued to the surface of the earth.

In my letter of April 22 I illustrated my point by considering the analogy with the case of ionised air between two parallel plates maintained at a constant difference of potential. As this comparison is inaccurate, I shall take the liberty of putting the case in another way, in the hope that it may prove more convincing. The earth is to be regarded as a conducting sphere which is continuously receiving a negative charge in certain areas—probably those in which rain is falling—and losing it again by conduction through the atmosphere from all the rest of its surface. Since the observations on the earth's field only refer to fine-weather regions, we need only consider what happens over them. There will be an earth-air current which, under specified conditions, will have attained a steady value, the charge on the earth's surface being that required to give the necessary potential gradient to drive the current. Suppose that by some means the ionisation at some distance from the surface suffers a permanent increase locally, whilst the air close to the surface is unaffected. It is clear that, whatever view is

taken of the distribution of the charges producing the earth's field, the increase in the ionisation will produce a local increase in the earth-air current; but by hypothesis the conductivity of the air close to the earth is unaltered, so that the increase in the current must be accompanied by an increase in the potential gradient close to the surface. This is, of course, produced by negative electricity flowing from other parts of the earth.

The above, I imagine, is an exaggerated but otherwise trustworthy picture of the effect an ionising radiation from outside would have on the earth's electric field. The conductivity produced by the rays in the upper atmosphere must be enormous compared with the effects close to the earth. Even if the rays were homogeneous, only a mere trace would remain after passing through a layer of air roughly equivalent in absorbing power to 76 cm. of mercury. But it is far from probable that they are homogeneous, and any want of homogeneity would exaggerate the effect. Other factors conspire to this end: the presence of dust near the earth loading the ions and the smaller rate of recombination at low pressures; whilst the increase in the mobility of the ions at low pressures would just compensate for the feeble absorbing power of the upper atmosphere.

It will be observed that the effect on the earth's field of an increase in the ionisation of the atmosphere depends entirely on where that increase takes place. If the conductivity increases in a greater ratio close to the earth's surface than it does further away, the result ought to be a fall in the potential gradient. Mr. Simpson rightly points out that such a relation between the potential gradient and the leakage of electricity near the earth's surface has been shown to exist. From my point of view this indicates that the bulk of the ionisation near the earth's surface is not caused by radiation from an external source.

O. W. RICHARDSON.

Trinity College, Cambridge, May 12.

Defects in Ostrich Feathers in South Africa

THE domestication of the ostrich on a practical basis was undertaken in Cape Colony about 1867, and since then ostrich farming has become one of the most important industries in the eastern province. The census of 1904 gave 357,970¹ tame ostriches in the colony, while the export of feathers reached 470,381 pounds, practically the whole of which came from tame birds; the estimated value of the feathers was 1,058,988l., giving about 3l. 10s. per bird of feather-producing age. During the forty years of domestication the instincts of the ostrich have apparently undergone no change, though its habits are much altered. The feathers cut from the tame bird are shorter, weaker, and not so fluffy as those taken from wild birds, but probably these differences are to be correlated with the greater frequency of plucking, and not with any constitutional change resulting from domestication.

Within recent years much concern has arisen from the prevalence of a defect in the growth of the feather, which seriously reduces the value of the plumes to the farmer. The imperfection, technically known as "barring," takes the form of a series of narrow, chevron-shaped bars or malformations across the whole feather. The general appearance of a moderately affected plume is shown in the accompanying photograph (Fig. 1). Examined closely, it is seen that the regularity of the individual barb is much disturbed at the bars, and that the barbules are there defective and only partly differentiated from the barbs. The appearance is such as to suggest that the barbs have been constricted at these particular regions, and that in the development of the feather the barbules have failed to become differentiated and open out, though with a needle their separation can sometimes be effected. Occasionally several barbs will remain joined together at the bars, they also having failed to differentiate. In many cases some of the barbs are shortened, the missing part having broken

¹ The statistics are taken from a paper, by the Hon. Arthur Douglass read before the recent meetings of the British Association at Cape Town. Mr. Douglass is the author of a well-known work, "Ostrich Farming in South Africa," and was one of the pioneers in the domestication of the ostrich, and probably the first to hatch the chicks by artificial incubation. His death, shortly after the meetings of the Association, is a great loss to the agricultural and political life of Cape Colony.